

**Close out and Final report for
NASA Glenn Cooperative Agreement NCC3-763**

**Factors Controlling Elevated Temperature Strength Degradation of
Silicon Carbide Composites**

Summary of Work

For 5 years, the cooperative agreement NCC3-763 has focused on the development and understanding of SiC-based composites. Most of the work was performed in the area of SiC fiber-reinforced composites for UEET and NGLT and in collaboration with Goodrich Corporation under a partially reimbursable Space Act Agreement. A smaller amount of work was performed on C fiber-reinforced SiC matrix composites for NGLT. Major accomplishments during this agreement included:

- Improvements to the interphase used in melt-infiltrated (MI) SiC/SiC composites which increases the life under stressed-oxidation at intermediate temperatures referred to as “outside-debonding”. This concept is currently in the patent process and received a Space Act Award.
- Mechanistic-based models of intermediate temperature degradation for MI SiC/SiC
- Quantification and relatively robust relationships for matrix crack evolution under stress in SiC/SiC composites which serve as the basis for stress-strain and elevated temperature life models
- The furthering of acoustic emission as a useful tool in composite damage evolution and the extension of the technique to other composite systems
- Development of hybrid C-SiC fiber-reinforced SiC matrix composites
- Numerous presentations at conferences, industry partners, and government centers and publications in recognized proceedings and journals.
- Other recognition of the author’s accomplishments by NASA with a TGIR award (2004), NASA’s Medal for Public Service (2004), and The American Ceramic Society’s Richard M. Fulrath Award (2005).

The following will briefly describe the work of the past five years in the three areas of interest: SiC/SiC composite development, mechanistic understanding and modeling of SiC/SiC composites, and environmental durability of C/SiC composites. More detail can be found in the publications cited at the end of this report.

SiC/SiC Composite Development

SiC/SiC composites are comprised of three constituents: the *fibers*, which usually come in a tow of several hundred fiber that are woven into 2D cloth which is then stacked by the composite manufacturer into the desired shape and thickness, the *interphase*, which is usually a coating

deposited by chemical vapor infiltration (CVI), and the SiC *matrix*, which can come in several forms either via CVI and/or a combination of SiC-slurry infiltration, polymer infiltration, followed by molten Si infiltration. Figure 1 shows a picture of a typical 2D woven MI composite.



Figure 1. Typical SiC fiber-reinforced MI SiC matrix composite.

The interphase, though smallest in volume, is critical to composite performance because it enables separation of the fibers from the matrix. A good composite is one where the composite properties are dictated by the very strong fibers that are reinforcing it. In order for this to occur, the interphase must provide a weak layer between the fibers and the matrix so that when matrix cracks are formed, the fibers will debond from the matrix and act independent of it. In addition to the mechanical requirements, the interphase must provide some protection from the environment since SiC composites when in contact with oxygen or water vapor at elevated temperatures react to form solid oxide products which can fuse the fibers to the matrix resulting in composite strength degradation.

Unfortunately, due to processing, chemical, and mechanical property-requirements, BN is the best candidate material for the interphase. However, standard low-temperature deposited BN is very susceptible to oxidation and composite embrittlement. Therefore, two interphase concepts have been developed in the cooperative agreement to enhance elevated temperature performance of the BN interphase. First, a high deposition temperature BN coating doped with a high concentration of Si was developed and able to be coated to 2D woven cloth. The coating showed significant improvements in resistance to oxidation. However, it is difficult and costly to produce and only reached the proof of concept stage.

A second approach involved the standard BN interphase; but, the interface of debonding was engineered so that debonding occurred between the BN and the SiC-matrix composite (outside debonding) rather than the typical SiC-fiber/BN interface (inside debonding). Figure 2 shows the difference in fracture between the two types of interphases.

Outside debonding composites proved to significantly improve the toughness and intermediate temperature environmental durability of SiC/SiC composites. Figure 3 shows the relative stress-rupture properties at 815 °C for composites developed under NASA's EPM and UEET programs and the improvement in rupture properties for outside debonding composites. Various composites were fabricated to modify and understand the nature of debonding and the effect on composite properties. A patent was applied for (LEW 17,240-1) and is now under review. Some

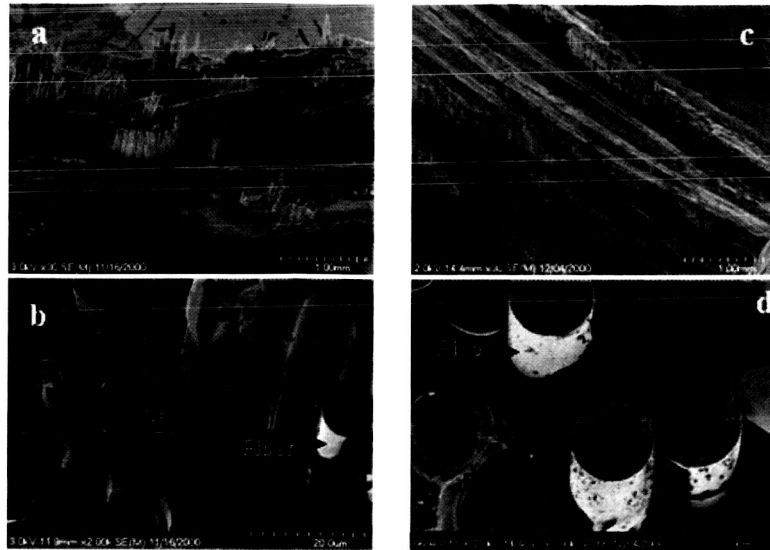


Figure 2. FESEM images of fracture surfaces of SYL-iBN composites showing outside debonding (a, b) and inside debonding (c, d).

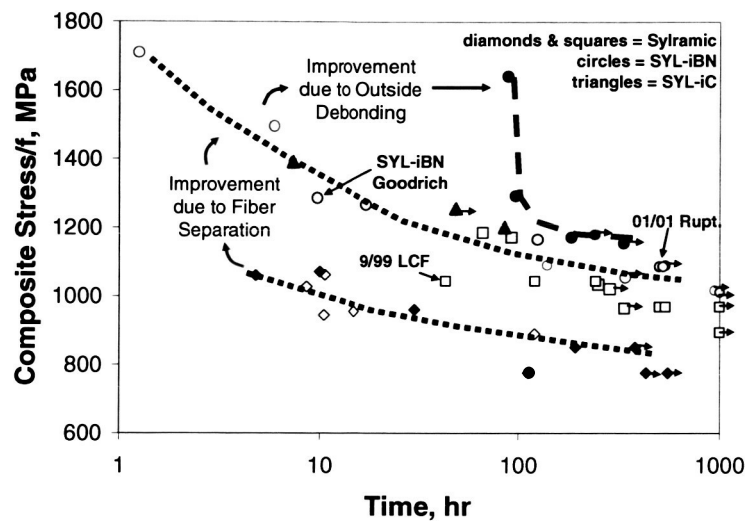


Figure 3. Stress-rupture of SiC/SiC MI composites at 815 °C plotted as the composite stress divided by the volume fraction of fibers in the loading direction.

of this technology was also transferred to Goodrich Corporation under a partially-reimbursable Space Act Agreement.

Further composite development was pursued under the Goodrich SAA with regards to composites reinforced with different fiber-types and matrix compositions. Some of these results were reported in Morscher and Pujar (2004).

Mechanistic Understanding and Modeling of SiC/SiC Composites

Two primary aspects of the mechanisms governing composite performance were investigated under this program. First, the intermediate temperature properties were modeled for two different SiC composites. The need for understanding the damage evolution in these types of composites in order to model elevated temperature properties then compelled the second area, understanding the evolution of matrix cracks in different SiC/SiC composites.

Intermediate temperature strength-degradation was modeled for a Hi-NicalonTM and Sylramic[®] fiber-reinforced 2D woven MI composites (see Morscher and Cawley, 2002). This was a refinement to Morscher's PhD Thesis (2000). The model was mechanistic, i.e., depicted the process of damage evolution and strength degradation that occur in these composites at intermediate temperatures in air. This necessitated careful examination of specimens which had failed. A number of factors were found to contribute to strength-degradation, most notably the reaction of the oxidizing environment with the BN to form solid oxide products which fuse the fibers to one another and the matrix. This would be controlled by the kinetics of oxygen ingress from the composite surface into a matrix crack and the reaction of the oxygen and H₂O with BN volatile H-B-O species and the formation of solid SiO₂ which replaces the BN and strongly bonds fibers to one-another and to the matrix. Since the nature of fiber failure was probabilistic, another key factor was the number of matrix cracks. The greater the number of matrix cracks, the greater the number or lengths of fibers that were exposed to the environment. Taking into consideration these factors as well others resulted in very good correlation between the model predictions and the actual stress rupture behavior (Figure 4).

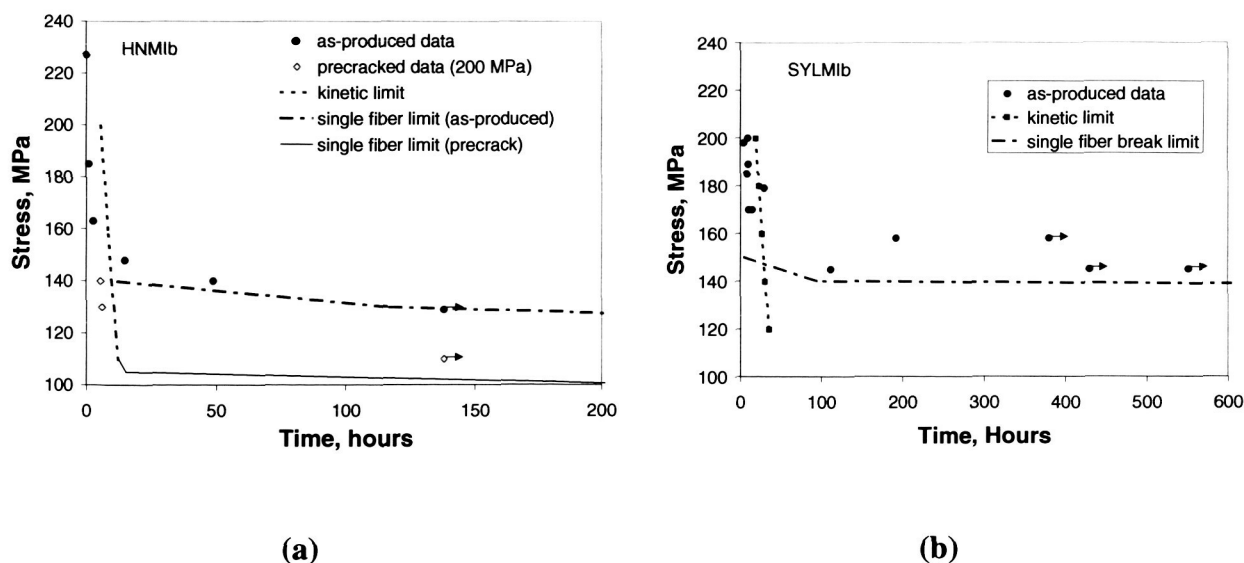


Figure 4. Stress-rupture at 815 °C in air of BN interphase composites with (a) HN fibers and (b) SYL fibers and model predictions.

The second area of understanding and modeling was stress-dependent matrix cracking in SiC/SiC composites. This was the dominant area of interest for the entire program and involved study into many different composite systems which incorporated variations in fiber-type, interphase, matrix, fiber architecture, composites with notches and composite shape. The approach was entirely based on modal acoustic emission and has resulted in this technique being a very important tool in the understanding of ceramic matrix composites. The primary references for this is the *Comp. Sci. and Tech.* (2004) paper for 2D woven MI composites and the *J. Am. Ceram. Soc.* (2005) paper for the 3D architecture MI composites. The approach was more recently applied to CVI SiC composites which has recently been written up as a paper and submitted to *Comp. Sci. and Tech.*

The basic technique involved monitoring the AE of composites tested at room temperature for stress-strain behavior. After the composites were tested, usually to failure, the composites were cut and polished in order to measure the matrix crack density and then compared with AE. Many different specimens with varying constituent content, tested to different stresses were performed in order to validate the relationships between AE and matrix cracking. The result was a simple relationship for 2D woven MI composites between stress and matrix crack density when the effect of constituent content and properties on the elastic modulus of the specimen were factored in.

Figure 5 shows the stress strain behavior and AE behavior for several 2D woven standard tow size MI composites. Note that Hi-Nicalon and Sylramic-iBN fiber-reinforced composites are shown. There is a significant variation in the “shape” of the stress-strain curves and the stress-range where AE or matrix cracking occurs.

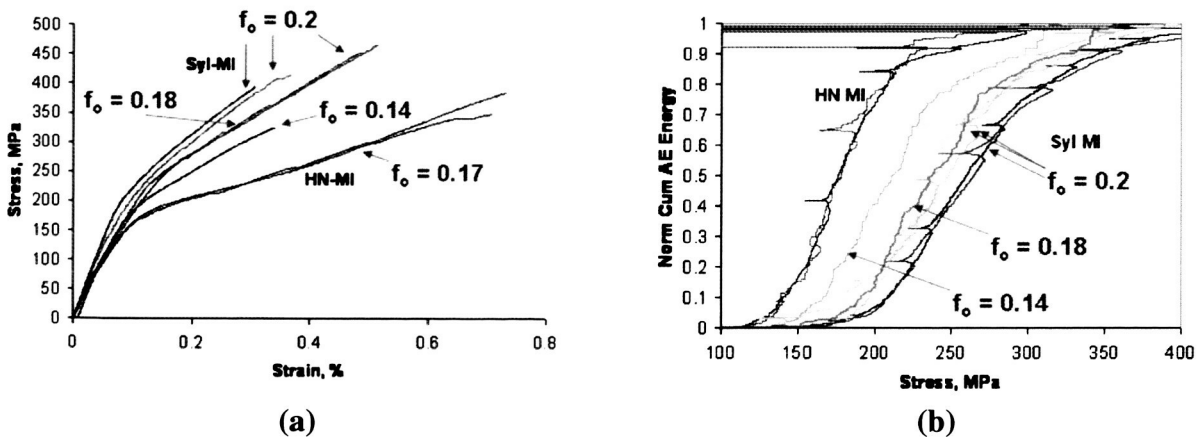


Figure 5. Stress-strain (a) behavior and AE activity (b) for several 2D woven MI composites.

However, from the findings in this study, the source of matrix cracks was shown to be the 90° fiber-tow minicomposites and a simple relationship could be found that related matrix cracking to the stress that the 90° minicomposites are subjected to. This stress, deemed, the “minimatrix” stress is a simply dependent on constituent contents and properties:

$$\sigma_{\min i matrix} = \frac{(\sigma_c + \sigma_{th})}{E_c} \left(\frac{E_c - f_{\min i} E_{\min i}}{1 - f_{\min i}} \right) \quad (1)$$

where σ_c is the stress on the composites, σ_{th} is the residual stress inherent to the composite due to thermal mismatch between the constituents, E_c is the composite elastic modulus, $f_{\min i}$ is the fraction of fibers, interphase, and CVI SiC associated with a minicomposite, and $E_{\min i}$ is the elastic modulus of the minicomposite in the direction of the fibers. When all the data of Figure 5b is plotted versus $\sigma_{\min i matrix}$ a simple probability function results for the 2D woven composites when tested in the fiber direction. One could then use the best-fit Weibull relationship for any 2D MI composite to model the stress strain behavior of that composite, e.g., Figure 6. Also, the onset of significant matrix cracking can be determined for any 2D MI composite from the curve which becomes a critical design parameter for these types of composites since the stress at which significant composite strength-degradation occurs is associated with the onset of large matrix cracks.

This same approach was applied to 3D orthogonal composites where the z-direction fiber was varied (see Morscher, Yun, and DiCarlo, 2005). It was found that the AE technique was able to decipher matrix cracking in different regions of the architecture accurately. This demonstrated the effect of architecture on matrix cracking. For regions similar to 2D 0/90 composites, the same relationship applied as in Figure 7. However, for other regions where z-fibers were perpendicular to the applied stress, the thickness of the z-fiber

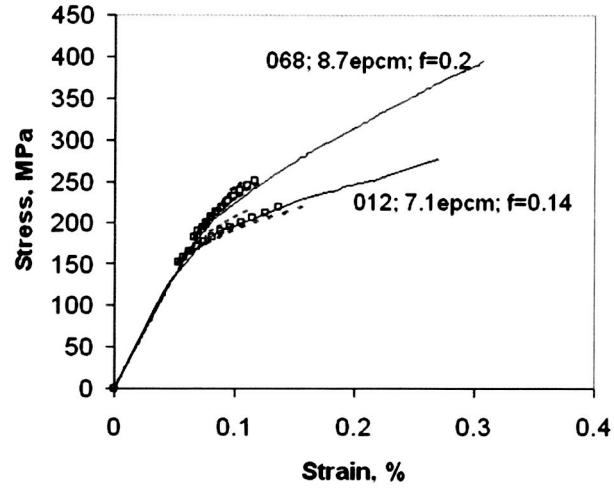


Figure 6. Model predictions of stress-strain behavior from relationship for matrix cracking shown in Figure 7.

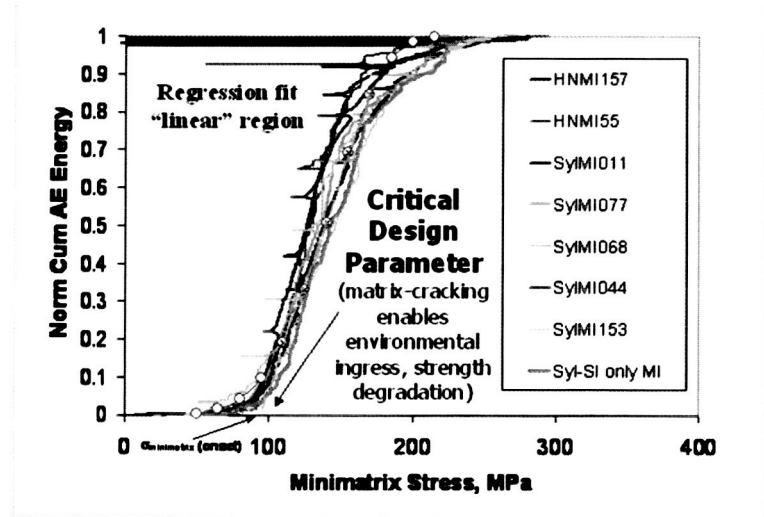


Figure 7. AE behavior of 2D woven MI composites plotted versus minimatrix stress.

For regions similar to 2D 0/90 composites, the same relationship applied as in Figure 7. However, for other regions where z-fibers were perpendicular to the applied stress, the thickness of the z-fiber

minicomposite dictated the stress at which matrix cracking occurred. In addition, other 2D composites with a different tow size resulted in different matrix cracking properties which must be factored in if using those types of woven architectures.

This type of modeling has also now been extended to CVI SiC matrix composites. In this system, since the composites consist of large amounts of porosity between minicomposites, the controlling matrix cracking parameter is the elastic modulus of the CVI SiC. For example, in the Sylramic-iBN fiber composites Figure 8 shows the stress-strain behavior and the AE behavior.

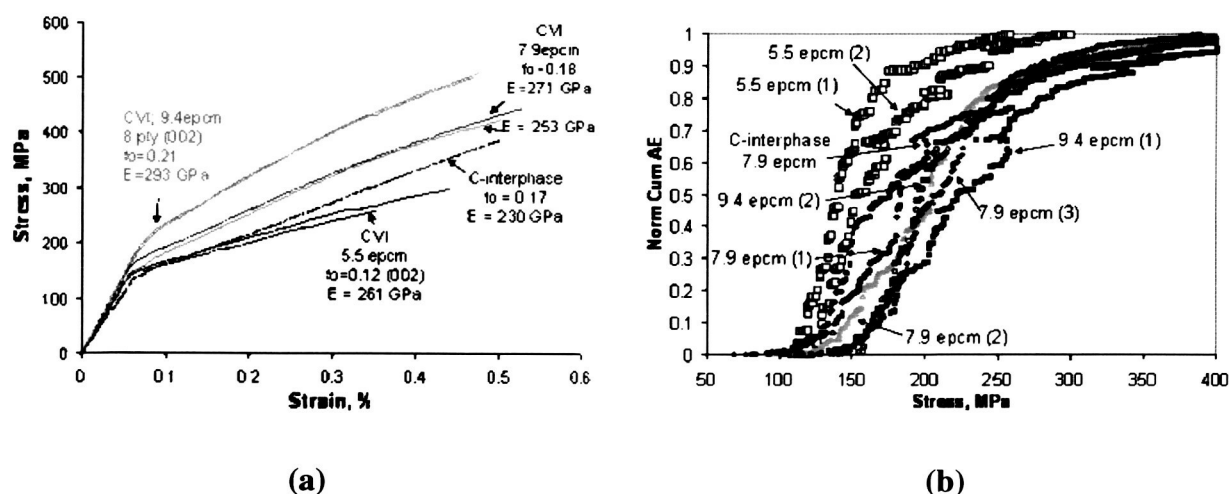


Figure 8. Stress-strain (a) behavior and AE activity (b) for several 2D woven CVI composites.

Note that different 2D weaves were used in this study. Some were “balanced,” i.e., the same number of fiber tows were woven in one direction as the other. However, others were “unbalanced,” i.e., more fiber tows were woven in one direction compared to the other. The composites with the most fibers in the loading-direction have the highest strengths and higher stresses necessary to cause matrix cracking. The “minimatrix” approach was attempted but was found not to represent matrix cracking in any general way. One reason for this is that in MI composites there is very little porosity, but in CVI SiC porosity is at least on the order of 15% and the nature of the porosity results in sharp notches near where the 90° and 0° tows overlap. This is the most severe flaw source and is not present in MI composites. It was reasoned that the CVI SiC is the material that has to allow matrix cracks to proceed whether at a notch or those that form in 90° bundles, therefore, the data was analyzed on the basis of the stress in the CVI SiC (Figure 9) and was found to be a good parameter for modeling matrix cracking in this composite system.

Note that two matrix cracking relationships exist: one for composites with a higher volume fraction of fibers in the loading direction (higher ends per cm, epcm, in the loading direction) and one for the composites with a low epcm in the loading direction. The reason for this is due to the flaw size for matrix cracking and the number of fibers available to “bridge” and slow down matrix cracks. For the low epcm composites, they were “unbalanced” so that more fibers were aligned perpendicular to the loading direction compared to the loading direction. This resulted in

more 90° tows which were often aligned so that two or three 90° tows were adjacent to one another with no 0° tow separating them. This results in a very wide matrix crack that can form which has no 0° fiber bridging whatsoever over that length, i.e., a very large flaw. In addition, the concentration of 0° fibers available to bridge matrix cracks is much less for the low fiber volume fraction composites resulting in a different matrix cracking distribution as evident in Figure 9. Again, these matrix cracking relationships were used to model stress-strain behavior effectively.

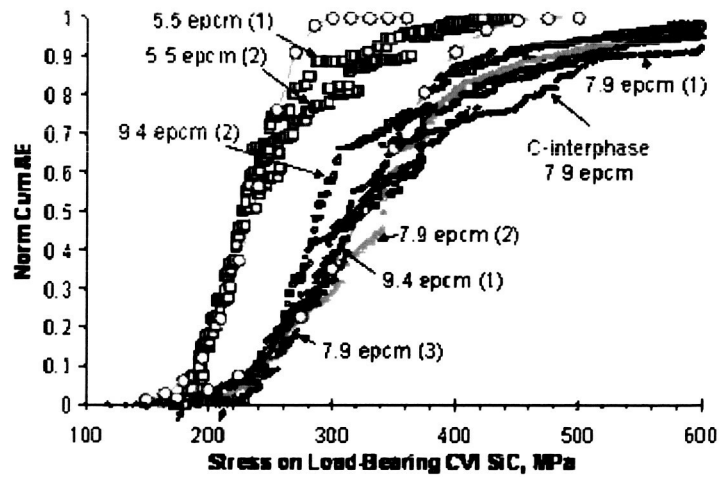
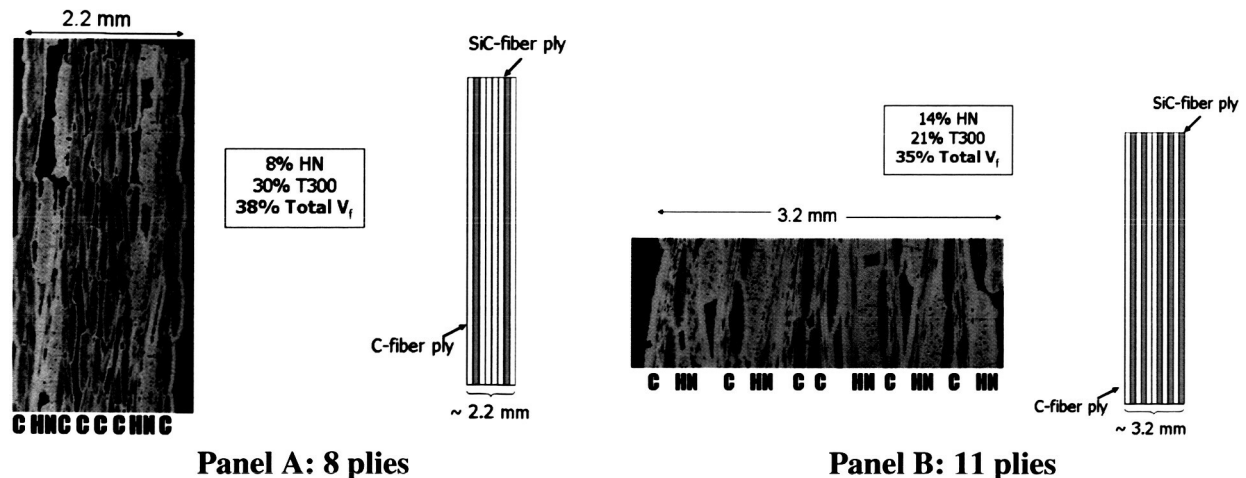


Figure 9. Relative AE activity in 2D woven Sylramic-iBN CVI SiC composites.

Environmental Durability of C/SiC

Various Carbon fiber reinforced SiC matrix composites were fabricated in order to enhance the durability of these composites in oxygen containing environments. Various BN interphases were attempted similar to the work done in SiC/SiC composites without much success. A more successful approach was to add woven SiC fiber layers into the C/SiC composite in order to use the SiC/SiC layer as an oxidation barrier. A couple variations were processed after some delamination issues (Figure 10). Panel A consisted of only two layers of SiC compared to six layers of C whereas panel B consisted of five layers of SiC compared to six layers of C. Note that the woven C layers had more fibers per layer than the woven SiC fiber layers.



Panel A: 8 plies **Panel B: 11 plies**
Figure 10. Two different hybrid C+SiC layer SiC matrix composites.

Significant stiffening was observed in these composites when compared to standard C/SiC composites (Figure 11). This stiffening was due to higher elastic modulus SiC fibers and fewer matrix cracks. However, there were matrix cracks present even in the SiC/SiC plies after fabrication. There was some improvement in the environmental durability properties of the hybrid composites at low stresses and temperatures with increasing SiC fiber content (Figure 12). However, there was little improvement over standard C/SiC composites when the composites were coated with GE's proprietary CBS external coating when compared to standard C/SiC composites coated with the same CBS coating (Figure 12). Funding for this research was stopped prematurely with the cancellation of the NGLT program.

Collaborators

This work could not have been performed without the collaboration of many NASA and NASA-affiliated coworkers. These include James A. DiCarlo, Ram Bhatt, Fran Hurwitz, J. Douglas Kiser, Hee Man Yun, Mrityunjay Singh, Andrew Gyekenyesi, and many others associated with the Ceramics Branch of the Materials Division and Structures Division at NASA Glenn.

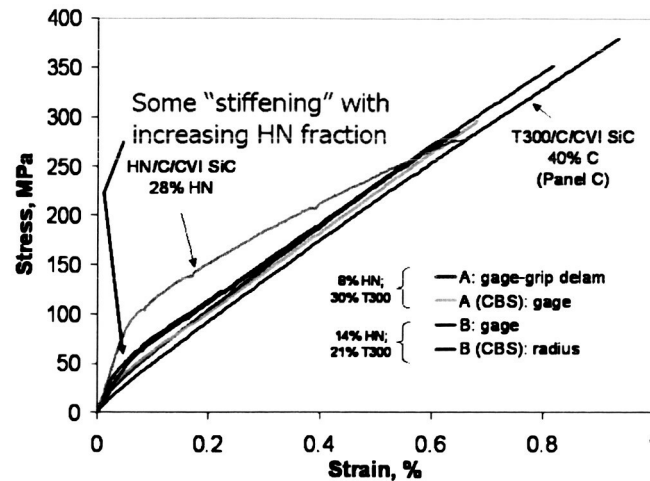


Figure 11. Stress-strain behavior of C-SiC, SiC/SiC, and hybrid composites.

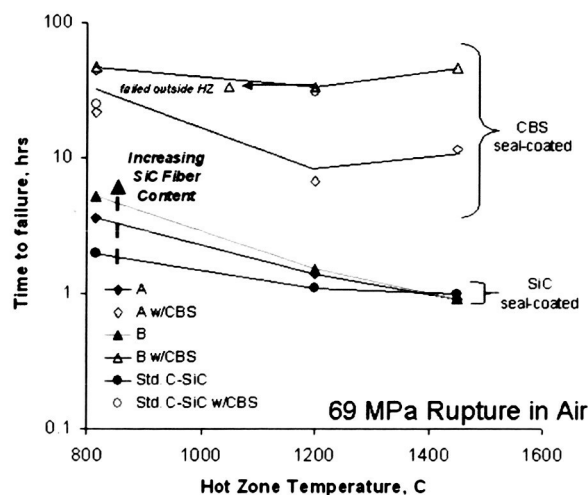


Figure 12. Rupture time for composites stressed at 69 MPa in air.

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